

Heavy Metal Mobility in Incinerator Ash Coastal Landfill

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Synopsis

The natural attenuation process of heavy metals in landfill waste layer and clay liner depends on factors such as the pH, Eh, Total Organic Carbon (TOC), microbial activities, and certainly, on the waste material that generates the leachate. These factors can change in the long term affecting the containment and attenuation process of heavy metals within the landfill. This study investigates the mobility of heavy metals, in particular zinc, in the incinerator ash layer of a coastal landfill site by conducting a large-scale column test. Test results indicate that pH and Eh are the main factors that influence the solubility of Zn, and microorganisms only play a minor role. After 7 months, the values of pH and Eh stabilized at levels where soluble Zn were not detected; however those values are close to the limits where mobilization is expected.

Keywords: heavy metals, landfill, incinerator ash, marine clay liner, pH

1. Introduction

In Japan, coastal areas are being utilized as landfill sites due to limited inland space. Coastal landfill sites commonly use natural marine clay layers as bottom liners. The current regulation permits that a natural clay $\geq 5\text{m}$ in thickness with hydraulic conductivity $\leq 1 \times 10^{-5} \text{ cm/s}$ could be utilized as liner. However, this regulation does not specify the methods to measure the hydraulic conductivity, and little research has been published on the applicability of marine clay as a liner, despite the popularity that coastal landfilling has attained nowadays in the metropolitan areas of Japan (Kamon and Katsumi, 2001).

Leachate from landfills contains many dissolved and suspended substances that are detrimental to the quality of the waters and to the geotechnical performance of clay liners. To control the heavy metals present in leachate is crucial because they

possess biological toxicity. The natural attenuation process of heavy metals in landfill including clay liners depends on factors such as the pH, Eh, Total Organic Carbon (TOC), microbial activities, and on the waste material from which the leachate is generated. These factors vary during the lifespan of a landfill affecting the containment and attenuation process of heavy metals through time.

Since the characteristics of the leachate coming into the clay layer will depend on the performance of the waste layer, it will be of great significance to understand the attenuation effects of the incinerator ash layer on the heavy metal behavior. In the long term, this study will determine the effectiveness of the current liner system in the pollution protection of the Japanese coastal sites.

2. Background

Natural attenuation processes take place within

the bottom clay liner reducing the concentration of leachate parameters by the following attenuation mechanism: (1) adsorption, (2) biological uptake, (3) cation and anion exchange, (4) dilution, (5) filtration, and (6) precipitation reactions. All this attenuation mechanisms depends on factors such as: leachate velocity, the degree of saturation which will influence biological uptake and precipitation reactions, and organic and inorganic matter present in the ash and clay layers (Bagghi, 2004).

Zinc was selected as target pollutant because is generally found in the leachate from both hazardous and municipal solid waste (Kamon et al., 2000) and it shows a similar behavior to other heavy metals such as lead. In the case of Zn, the major attenuation mechanisms are adsorption, cation-exchange, and precipitation, and its mobility has been found to be rapidly affected by increases in pH from 2 to 8, with a significant drop between 6 and 8. Therefore Zn attenuation will be most favored by an alkaline condition (Bagghi, 2004).

Bottom Clay liners used at coastal landfills may be under moderate to alkaline conditions, but the incinerator waste layers will suffer pH variations during the lifespan of the coastal landfill site affecting the chemical composition of leachate and favoring at times the mobilization of Zn and other heavy metals. The chemical composition of leachate will change greatly depending on the age of landfill. If a leachate sample is collected during the acid phase of decomposition, the pH value will be low and the concentrations of Biochemical Oxygen Demand (BOD₅), TOC, Chemical Oxygen Demand (COD), nutrients and heavy metals will be high. If, on the other hand, a leachate sample is collected during the methane fermentation phase, the pH will be in the range from 6.5 to 7.5, and the BOD₅, TOC, COD, nutrient concentration and heavy metal concentrations will be significantly lower (Tchobanoglous et al., 1993).

There are speculations that the methane fermentation phase will be followed by a mature aerobic phase (Zhang et al, 2004). During this phase the air will begin to penetrate within the waste cell, turning the established anaerobic condition into an aerobic one, and this condition might lead to a drop in pH values favoring the mobilization of heavy metals.

3. Experimental Method and analysis

3.1. Materials and Methods

A large-scale column test was chosen to simulate the conditions of a coastal landfill site and study the soil-pollutant interactions on a marine environment. Column test are appropriate to replicate solute movements through the soil pores and the sorption of metals on soil particles (Harter et al., 2001)

A large-scale column test was carried out during 345 days to evaluate the relationship between pH, Eh, TOC and microbial activities with the mobility of heavy metals within the incinerator ash layer. Figure 1 shows the experimental set up employed for this research. The column with 190 mm in inner diameter and 1,500 mm in height is made of acrylic resin and it has 10 sampling points. Marine clay sampled from Osaka Bay was prepared with 150 mm height at the bottom of column. Then, incinerator ash collected from the incinerator plant for the municipal solid waste was placed on the clay layer with 850 mm in height. The basic properties of the Osaka marine clay are shown in Table 1.

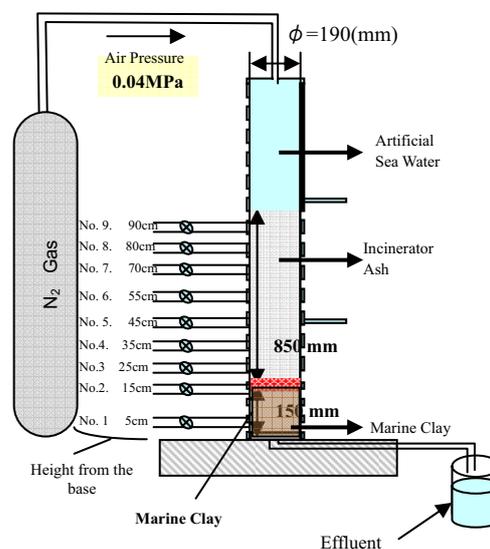


Fig. 1 Scheme of experimental set up

Table 1 Basic properties of Osaka marine clay used.

| | |
|---------------------------------------|------|
| Particle Density (g/cm ³) | 2.61 |
| Liquid Limit (%) | 41.1 |
| Plastic Limit (%) | 26.7 |
| Ignition Loss (%) | 6.01 |
| pH | 8.87 |

The experiment set up included the preparation of artificial sea water, enhanced with 2000mg/l of $ZnCl_2$; 1000mg/l of $NH_4H_2PO_4$ and 1000mg/l of Na_2SO_4 , which were added to favor reduced conditions. After these adjustments, the pH of the influent was approximately 5.1.

The marine clay employed in this study was consolidated under a consolidation pressure of 200 kPa, representing an approximate overburden pressure of disposed solid waste at a 20 m depth.

The column was continuously bubbled with N_2 gas during the time of the experiment under a pressure of 0.4MPa.

3.2. Measurements and Chemical Analysis

Along the waste layer and the marine clay layer, pore water was sampled from 9 different sampling ports shown in Fig. 1. The influent (artificial sea water) and the effluent from the bottom were periodically sampled as well.

The pH and Eh were measured immediately after sample collection. Then, the samples were filtered with a 0.45 μm pore size filter. The total organic carbon (TOC), Sulfide and Zn concentration of the filtered solution were analyzed by a Total Organic Carbon Analyzer (TOC-5050A, Shimadzu), UV Visible Spectrophotometer (UVmini – 1240, Shimadzu) and inductively coupled plasma spectrophotometer (ICPS-8000, Shimadzu), respectively. As an index of the microbial activity in the system, the total adenosine triphosphate (ATP) concentration was determined by the relative light unit value (RLU) using ATP analyzing system (Aquatrace system, Biotrace).

4. Test Result and Analysis

4.1 pH and Eh behavior

Figure 2 shows the pH distribution change along the column with time. During the first 50 days, the pH dropped dramatically at the top of the incineration waste layer (No.9) and at point No. 8 the fall in pH was significant but less severe. From point No.7 to No.1, pH only presented slight variations proving the high buffer capacity of the incineration ash. At the surface level (No.9) values of $pH \leq 7$ were observed, while at the bottom, alkaline conditions remained through the experiment. With time elapsed, pH is

gradually dropping from the top surface of the incinerator ash layer since the continuous water flow promotes the leaching of alkaline.

Figure 3 shows the Eh distribution change along the column with time. Eh dropped dramatically at all depths during the first month. Initial Eh was about -150mV and it reached values below -500 after only 21 days. This rapid Eh dropping is considered to be caused by the leaching of various chemicals from the ash with high concentrations. After three months Eh values stabilized and started showing a minor increase. The increase took place at a faster pace at the top than at the bottom of the column. Between month 4 and month 7, conditions at point No.9 shifted from highly reduced (below -100mV) to reduced (from -100mV to 100mV).

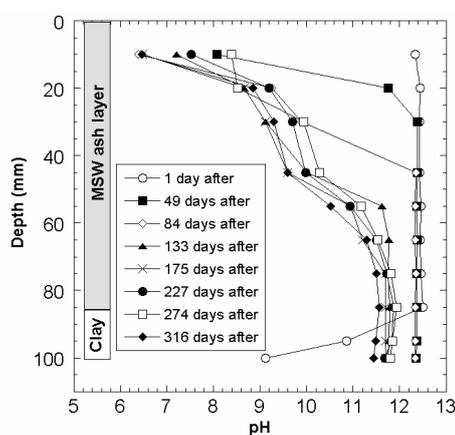


Fig. 2 pH variations in big column test

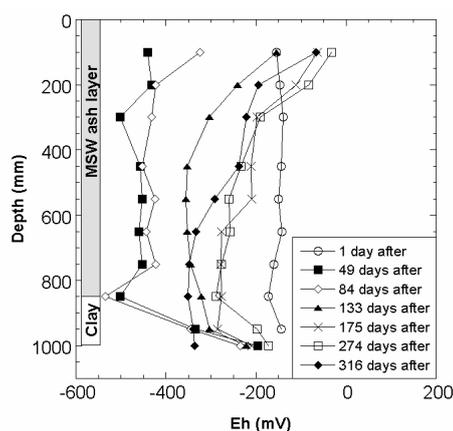


Fig. 3 Eh variations in big column test

4.2 Influential factors on zinc mobility

Although 2000mg/l of $ZnCl_2$ were added to the influent, no soluble Zn was detected out of any of the

sampling points along the large-scale column during the first 100 days of the experiments. As shown by Fig. 4, Zn concentrations in the order of 100ppm, were detected at point No.9 between days 100 and 200 of the experiment. This was the only sampled point where high concentration of Zn was detected during the experiment.

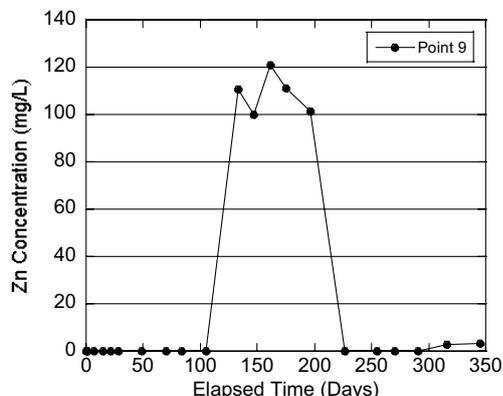


Fig. 4 Zinc fluctuations at Point No.9

At the time of Zn detection, the pH ranged between 6.23 and 6.88 at point No.9, and it remained above 7 at all the other points along the column. In addition, Eh values at point No.9 showed their higher value, reaching very moderate reduced conditions.

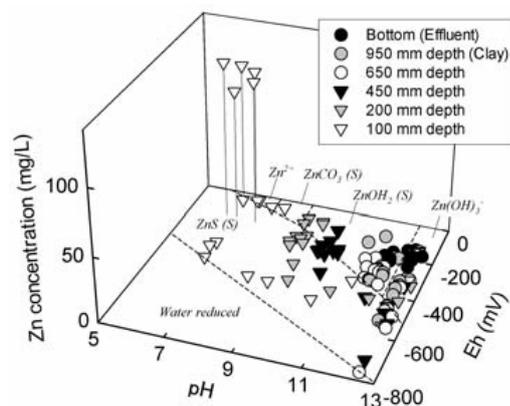


Fig. 5 Experimental results of Zn concentration and pH-Eh diagram presented by Hem (1972)

Figure 5 shows Zn concentrations as functions of pH and Eh along the column test with the Zn forms expected for various pH and Eh values presented by Hem (1972). This result reveals that both pH and Eh influence the mobility of Zn in soil-system. As pH decrease and Eh increase, Zn is dissolved in water. In contrast, when pH increases and Eh decreases greatly, Zn is effectively immobilized in soil.

4.3 Relevant observations

Figure 6 shows a low but constant production of sulfide during the experiment. The presence of sulfide indicates that sulfate reduction is taking place. Figure 5 illustrates that, under strongly reduced conditions, especially at sulfate reduction stage; the reduced products of sulfate will react with soluble zinc forming zinc sulfide precipitations. Therefore, at certain times, the formation of zinc sulfide can be named responsible for the absence of soluble Zn.

At the beginning of the experiment there was a rapid decrease in the TOC concentration. This occurs because the oxidation of organic compounds under aerobic conditions occurs at a higher rate than under anaerobic conditions. As a result, a decrease in pH is observed (see Fig.2 and Fig.7). This data shows that oxidation of organic carbon leads to an acidification process.

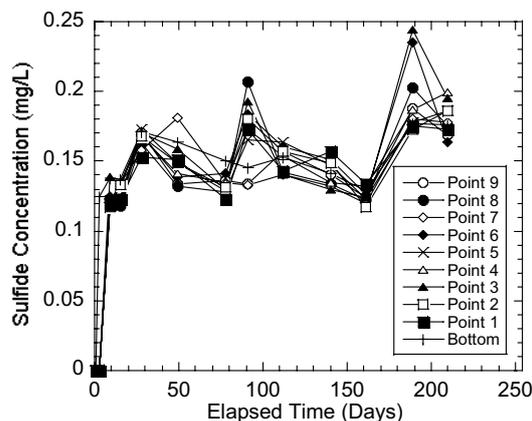


Fig. 6 Sulfide variations during big column test

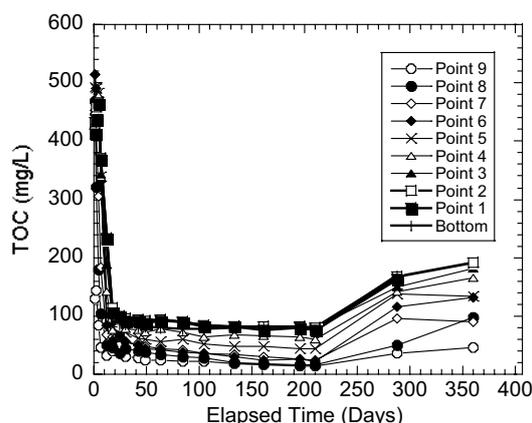


Fig. 7 TOC variations in big column test

From the ATP variation shown in Fig.8, microbial activity starts increasing after 100 days, and

at point No.9 microorganisms show relatively higher activity during the days that Zn was released, but despite their constant growing, their activity is not enough to further affect pH and Eh and Zn was not measured again during the time of the experiment (see Fig. 8).

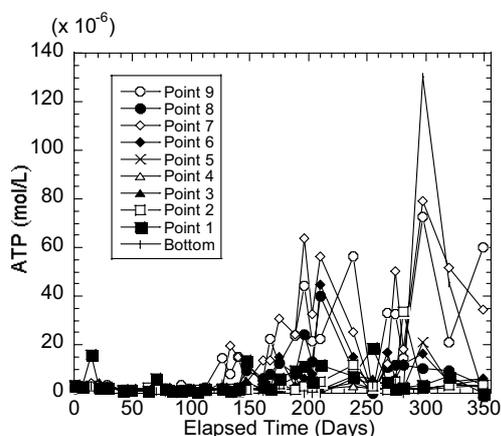


Fig. 8 ATP variations in big column test

4.4 Further Studies

This research has been focus, up to now, in the measurement of the total concentration of heavy metal as criteria to evaluate the attenuation mechanisms that take place within a coastal landfill site. To measure the total metal concentration suppose that all forms of a given metal have the same impact on the environment and display the same behavior as factor such as pH, Eh and TOC varies in time. In order to have a better understanding of the attenuation mechanisms of leachate within a coastal landfill it is recommendable to partition heavy metals into specific fractions which can be extracted selectively by using appropriate reagents.

From the data that has been obtained it is possible to infer that absorption and precipitation take place within the incinerator ash layer. As pH and Eh stabilized the concentrations of sulfide increase and zinc precipitates as ZnS and under moderated reduced condition Zn can be associated with Carbonates (see Fig. 5), however further information is required to support these statements. The next step of this research is to examine the different forms and concentration of zinc present along the large-scale column. Ash samples from various depths will be tested following a sequential extraction procedure, in order to obtain detailed information about the mode

of occurrence and biological and physicochemical availability of zinc to have a better understanding of the conditions that favor the mobilization of heavy metals.

5. Conclusions

Based on the experimental results, the following conclusions can be made on the heavy metal mobility in incinerator ash coastal landfill;

- [1] pH is the main factor that controls the solubility of Zn, since concentration of soluble Zn in the effluent were only detected when pH was around or below 7. Test results indicate that the lower the pH decreases, the more Zn is released.
- [2] In acid and moderately reduced conditions, zinc existed in soluble ionic form; but in neutral and weak alkaline conditions zinc precipitated out from solutions as insoluble hydroxides and carbonates.
- [3] Microorganisms only play a minor role, compare with the influence of pH and Eh, on the control of the mobility of heavy metals.
- [4] The increase in sulfide concentration might favor the heavy metal precipitation. Under sulfate reduction conditions, the formation of zinc sulfides might become another attenuation mechanism for zinc.
- [5] After 7 months the values of pH and Eh stabilized at levels where soluble zinc were not detected, however those values are close to the limits where solubilization is expected. Therefore, slight changes in the conditions of a coastal landfill might trigger solubilization of heavy metals and further studies on the long term behavior of coastal landfill sites are recommended.

Acknowledgement

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焼却灰埋立海面処分場における重金属の移動性

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要 旨

廃棄物処分場内部における重金属の移動性、緩衝作用は pH, Eh, 有機物、微生物活動に大きく影響され、埋立廃棄物の種類や時間経過によっても変化する。本研究では、焼却灰海面埋立処分場の廃棄物層、粘土層を模擬した大型カラム試験を長期に渡って実施し、処分場内部での重金属の移動性を亜鉛をトレーサーとして用いることにより評価を行った。試験結果より、重金属の移動性は pH, Eh による影響がみられるが焼却灰層内部に固定化されること、ならびに微生物活動の影響は非常に小さいことが明らかになった。7ヶ月経過時点で pH と Eh の値は安定しているが、亜鉛の移動性が高くなると推測される値に近い値となっており、今後も継続的な調査を実施する予定である。

キーワード：重金属、廃棄物処分場、焼却灰、海底粘土層、pH